

# PATENT APPLICATION

**TITLE:   PROCESS TO CONTROL NITROGEN-CONTAINING COMPOUNDS IN  
          SYNTHESIS GAS**

**INVENTOR:   JUAN INGA**

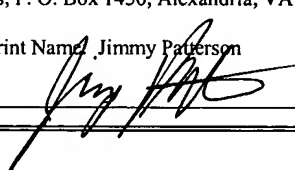
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PROCESS TO CONTROL NITROGEN-CONTAINING  
COMPOUNDS IN SYNTHESIS GAS

CROSS REFERENCE TO RELATED APPLICATIONS

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[1] Not applicable.

FEDERALLY SPONSORED RESEARCH

[2] Not applicable.

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REFERENCE TO MICROFICHE APPENDIX

[3] Not applicable.

FIELD OF THE INVENTION

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[4] The invention relates to a process to control the amount of nitrogen-containing compounds present in the synthesis gas feed to a Fischer-Tropsch process, and more particularly, to the use of a countercurrent flow of Fischer-Tropsch produced water to control nitrogen-containing compounds in an upstream Fischer-Tropsch reactor.

BACKGROUND OF THE INVENTION

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[5] Synthesis gas ("syngas") typically contains trace nitrogen-containing compounds, principally ammonia and hydrogen cyanide. Other reactive nitrogen compound species, such as cyanogen and nitrogen oxides, may also be present in very small amounts. Collectively, these nitrogen-containing compounds are referred to herein as N-contaminants.

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[6] N-contaminants arise from the presence of one or more nitrogen-containing species in the feed to the synthesis gas generator. For example, N<sub>2</sub> may be present in: (1) the feed natural gas; (2) the O<sub>2</sub> feed after air separation for an oxygen blown syngas generation process; and/or (3) the air or oxygen-enriched air feed for an air blown process. In addition to or alternatively to these sources of N<sub>2</sub>, nitrogen-containing hydrocarbon species (especially for liquid and/or solid syngas generation feedstocks, such as residual oil or coal) may also be present in the syngas generator. The concentration of N-contaminants produced in the syngas generator may also be increased substantially through the recycle of Fischer-Tropsch tail gas into the syngas generation process. Similarly, the concentration of N-contaminants produced in the syngas

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generator may also be increased by recycling of tail gases from other processes into the syngas generator.

[7] Virtually all commercially practiced and proposed syngas generation processes operate at extremely high temperatures, generally in the range of 1500°-2500°F, where the majority of the chemical reactions occur near or at chemical thermodynamic equilibrium. Under these conditions, small quantities of hydrogen cyanide (HCN) and ammonia (NH<sub>3</sub>) are typically produced. Yet smaller amounts of other reactive nitrogen-containing compounds, such as cyanogen, may also be produced. The amounts of HCN and NH<sub>3</sub> in a syngas depends strongly on both the nitrogen concentration in the syngas generator feed and the process conditions, particularly pressure and temperature. Typical concentrations of these nitrogen-containing compounds in the syngas generator outlet stream which has not been further processed (referred to herein as a "raw synthesis gas") are in the range from about 1 to about 50 vppm HCN and from about 5 to about 1000 vppm NH<sub>3</sub>. Generally, the raw syngas contains between about 10 and about 30 times more NH<sub>3</sub> than HCN.

[8] Ammonia, which is basic, is very soluble in water. Raw syngases contain both carbon dioxide and water vapor and at least about 90wt% of the ammonia present in the raw syngas can be removed by cooling the raw synthesis gas to less than about 200°F and condensing the produced water. CO<sub>2</sub> dissolved in the condensed water will facilitate dissolution of the ammonia from the synthesis gas. The amount of ammonia in the syngas may be further decreased by use of a water scrubber.

[9] HCN, on the other hand, is much less water soluble than NH<sub>3</sub>, and is somewhat acidic in solution. Therefore, HCN is much more difficult to remove by means of raw synthesis gas water knockouts and/or subsequent scrubbing. Removal by water scrubbing requires relatively large quantities of water, typically greater than 1:1 water:syngas mass ratios. Incremental HCN removal can be realized by recirculating the ammonia-containing wash water, produced by scrubbing the ammonia from the raw syngas which contributes to HCN disassociation and removal by water scrubbing. However, HCN removal with water scrubbing is inefficient, requiring excessive amounts of water in relation to the HCN quantity removed. A large number of known processes for HCN removal from synthesis gases, including HCN adsorption, catalytic conversion of HCN (hydrogenation and/or hydrolysis), and chemically treated water scrubbing of HCN are known. Other processes attempt to prevent the formation of HCN by

upstream removal of N<sub>2</sub> from natural gas. Such known processes, however, result in or require increased plant capital and/or operating costs, supply and disposal of treatment chemicals, and/or potential contamination of the treated synthesis gas. Moreover, many of these processes are hampered by the presence of other acidic materials, e.g. CO<sub>2</sub>.

- 5 [10] Removal of HCN and NH<sub>3</sub> from syngas is considered important because these nitrogen-containing compounds are poisons of Fischer-Tropsch catalysts, particularly non-shifting catalysts, and more particularly, those Fischer-Tropsch catalysts containing cobalt.

#### SUMMARY OF THE INVENTION

- 10 [11] Embodiments of the invention provide a process to remove N-contaminants from a synthesis gas stream including the steps of introducing a syngas stream and a water stream into a first absorber, recovering overhead from the first absorber a first-washed syngas stream, and introducing the first-washed syngas stream into a second absorber. A Fischer-Tropsch produced water stream is also introduced into the second absorber. Finally, a second-washed  
15 syngas stream is recovered from the overhead of the second absorber.

[12] In other embodiments of the invention, the second-washed syngas stream is used as a feed for a Fischer-Tropsch reactor. In some embodiments of the invention, the Fischer-Tropsch reactor utilizes a catalyst comprising cobalt.

- 20 [13] In some embodiments of the invention, the syngas stream is generated in the presence of air or oxygen enriched air.

- [14] Yet other embodiments of the invention provide a Fischer-Tropsch process including the steps of feeding a syngas into a first stage Fischer-Tropsch reactor and recovering a first overhead stream which contains Fischer-Tropsch water, hydrocarbon product and unreacted syngas, separating the unreacted syngas from the first overhead stream and feeding such  
25 unreacted syngas into a second stage Fischer-Tropsch reactor. A second overhead stream, which contains Fischer-Tropsch water, hydrocarbon product and unreacted syngas, is recovered from the second stage Fischer-Tropsch reactor, and the Fischer-Tropsch produced water is separated from the second overhead stream. The separated Fischer-Tropsch water is mixed with the first overhead stream.

- 30 [15] In some embodiments of the invention, the Fischer-Tropsch produced water is mixed with the first overhead stream before the unreacted syngas is separated from the first overhead stream. In yet other embodiments, the mixing of the Fischer-Tropsch produced water with the

first overhead stream occurs simultaneously with the separation of the unreacted syngas from the first overhead stream.

[16] In yet other embodiments of the invention, Fischer-Tropsch produced water is separated from the first overhead stream and is mixed with a raw syngas in an absorber to produce a washed syngas. In some embodiments of the invention, the washed syngas is used as a feed syngas to a first stage Fischer-Tropsch reactor

#### BRIEF DESCRIPTION OF THE DRAWINGS

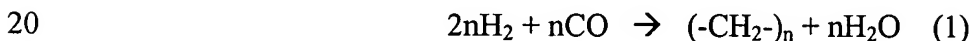
[17] Fig. 1 is a schematic of a first embodiment of the process of the invention.

10 [18] Fig. 2 is a schematic of a first embodiment of the absorption system for use in the process of the invention.

[19] Fig. 3 is a schematic of a second embodiment of the absorption system for use in the process of the invention.

#### 15 DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[20] The Fischer-Tropsch reaction for converting syngas, which is composed primarily of carbon monoxide (CO) and hydrogen gas (H<sub>2</sub>), is well known and may be characterized by the following general reaction:



Non-reactive components, such as nitrogen, may also be included or mixed with the syngas. This may occur in those instances where air, enriched air, or some other non-pure oxygen source is used during the syngas formation. The water produced according to Equation (1) above is referred to herein as "Fischer-Tropsch produced water" or as "FT produced water."

25 The hydrocarbon product of the Fischer-Tropsch reaction, as seen in Equation (1), is primarily composed of paraffins and olefins, with small amounts of oxygenates.

[21] Referring to Fig. 1, syngas 2 is fed into a first Fischer-Tropsch reactor ("FTR") 1. An overhead stream 5 is cooled using an aircooler 3 and optionally a water cooler 4. The cooled Fischer-Tropsch overhead stream 6 enters a first separator 7 where light hydrocarbons 18 and FT produced water 19 are separated. Overhead gases 8, which contain primarily unreacted syngas, enter a second FTR 9. A second Fischer-Tropsch stream 20 is recovered overhead from second FTR 9 and cooled by aircooler 10 and optionally further cooled by a water cooler or chiller 11. The condensed hydrocarbons 17 and FT produced water 13 present in the cooled

second Fischer-Tropsch stream 15 are separated in a second separator 12. A tailgas stream 16 may also be withdrawn from second separator 12. The tailgas 16 may then be used to fuel a turbine to produce power or may be passed into a third stage FTR to produce more hydrocarbon product. Alternatively, tailgas 16 may be otherwise recycled or disposed.

5 [22] Referring still to Fig. 1, the FT produced water 13, which was produced in second FTR 9 and collected in separator 12, is fed into and mixed with the cooled Fischer-Tropsch overhead stream 6 from first FTR 1. This mixing may be aided by the presence of an inline mixer or other appropriate mixing device, a number of which known.

[23] In some embodiments of the invention more than two FTRs may be used. In such  
10 embodiments, a water stream produced in an FTR may be cooled, separated and passed to one or more cooled product overhead streams from one or more FTRs upstream of the FTR in which the cooled water stream was produced. For example, a stream of Fischer-Tropsch water produced in a third stage FTR could be fed to the cooled second Fischer-Tropsch overhead stream 15.

15 [24] In yet other embodiments of the invention, the FT produced water 19 from the overhead separator 7 of first FTR 1 may be used to do a final rinse of syngas 2 upstream of the FTR 1. That is, the FT produced water made in any of the FTRs may be recovered, separated and fed upstream, i.e. countercurrent, to wash an FTR feed stream.

[25] Referring now to Fig. 2, a cooled raw syngas 21 is first washed in an absorber 22 with a  
20 water stream 23 that comes from a stripper column, or other water source, such as a makeup water supply. Raw syngas 21 may optionally be compressed prior to being washed in absorber 22. N-contaminants in raw syngas 21 are absorbed, in part, by the water stream 23. The absorbed N-contaminants exit the absorber 22 in a nitrogen-enriched aqueous stream 24, which may be sent to a stripper column wherein the nitrogen-containing compounds are separated  
25 from the water. The first washed syngas stream 25 may still contain low levels of  $\text{NH}_3$ , HCN and other N-contaminants.

[26] Syngas stream 25 may be further washed in second absorber 26 using Fischer-Tropsch  
produced water 27. Fischer-Tropsch produced water 27 typically contains very small amounts of  $\text{NH}_3$  and is acidic. Therefore, the Fischer-Tropsch produced water may facilitate the  
30 absorption of  $\text{NH}_3$  present in the syngas. The two-times washed syngas 28 may then be fed into a Fischer-Tropsch reactor. The nitrogen-enriched aqueous stream 29 recovered from the

second absorber 26 may be sent to a wastewater treatment process. Alternatively, the nitrogen-enriched aqueous streams 24 and/or 29 may be treated to remove nitrogen containments and recycled to the process. In some embodiments of the process, either or both of water stream 23 and Fischer-Tropsch produced water 27 may be temperature controlled to improve or modify the amount of nitrogen containments absorbed by such streams.

[27] In some embodiments of the process, the overhead effluent from first FTR 1 is not passed through either aircooler 3 or water cooler 4. In such embodiments, FT produced water 13 recovered from second separator 12 is cooled prior to being mixed with overhead stream 5. Water stream 13 may be cooled using any of a number of known methods. In some embodiments, water stream 13 is cooled by shell and tube water coolers. In some embodiments of the invention, Fischer-Tropsch produced water may be used as the wash water in one or both of the first and second absorbers 22 and 26.

[28] In yet other embodiments of the invention, absorbers 22 and 26 may be combined in a single vessel, with each absorber serving as a separate absorption zone within the vessel. In such embodiments, a bottom plate may be placed between the two absorption zones.

[29] Referring to Fig. 3, another alternative embodiment is shown in which the Fischer-Tropsch produced water 13 from second separator 12 is introduced directly into first separator 7, without prior mixing with the cooled overhead stream 6. Because water stream 13 is introduced above the gas/liquid separation, first separator 7 will behave as an absorber.

[30] Fischer-Tropsch produced water generally contains about 1 to 2 wt% of dissolved hydrocarbon oxygenates, including, for example, alcohols, ketones and acids. Such hydrocarbon oxygenates would enter either or both of absorbers 22 and 26, i.e. whichever absorbers in which FT produced water is used. Upon contact with the syngas stream, some or all such oxygenates may be vaporized and thus, exit the overhead of the absorber. Because the overhead of the final absorber is fed to an FTR, all or part of such oxygenates may be recovered in embodiments of the invention. For example, where FT produced water is used only in second absorber 26, all or part of the oxygenates may exit with two-times washed syngas stream 28 which is then fed into an FTR, most typically FTR 1.

[31] While presently preferred embodiments of the invention have been given for the purpose of disclosure, numerous changes in the details of construction, arrangements of parts and operation of the process can be made which will readily suggest themselves to those skilled

in the art and which are encompassed within the spirit of the invention and the scope of the appended claims.

[32] What is claimed is: